



**CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY**  
**DEPARTMENT OF TOXIC SUBSTANCES CONTROL**  
**Notice of Intent to Certify**  
**Hazardous Waste Environmental Technologies**

The California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) intends to certify the following company's hazardous waste environmental technology listed below:

Applicant: Space and Naval Warfare Systems Center, San Diego, CA 92512-5001  
Technology: Benthic Flux Sampling Device.

Health and Safety Code, section 25200.1.5, authorizes DTSC to certify the performance of hazardous waste environmental technologies. The purpose of the certification program is to provide an in-depth, independent review of technologies to facilitate regulatory and end-user acceptance. Only technologies determined not to pose a significant potential hazard to the public health and safety or to the environment when used under specified operating conditions may be certified.

DTSC makes no express or implied warranties as to the performance of the manufacturer's product or equipment. The end-user is solely responsible for complying with all applicable federal, state, and local regulatory requirements. Certification does not limit DTSC's authority to take any action necessary for protection of public health and the environment.

By accepting certification, the manufacturer assumes, for the duration of certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal to or better than was provided to obtain certification and agrees to be subject to quality monitoring by DTSC as required by the statute under which certification is granted.

DTSC's proposed decision to certify is subject to public review and comment. Written comments must be received by DTSC no later than 30 days after publication of this notice. All comments will be considered and appropriate changes will be made prior to publishing DTSC's final decision.

Additional information supporting DTSC's proposed decision, including the September 1, 1999 draft report, "*Quantifying In Situ Contaminant Mobility in Marine Sediments*" prepared by Space and Naval and Warfare Systems Center, San Diego, which describes the Navy's field testing procedures and results, is available for review at, and comments should be mailed to:

California Environmental Protection Agency  
Department of Toxic Substances Control  
Office of Pollution Prevention and Technology Development  
P.O. Box 806  
301 Capitol Mall, 1st Floor  
Sacramento, California 95812-0806  
Attn.: Dr. Bruce La Belle (916) 322-3670

A description of the technology to be certified, the proposed certification statement and the certification limitations for the technology of the company listed above follow. DTSC emphasizes that this is a proposed certification for public comment, and not the final certification.

**30-DAY PUBLIC NOTICE**  
**HAZARDOUS WASTE ENVIRONMENTAL TECHNOLOGIES**  
**PROPOSED TECHNOLOGY CERTIFICATION**

**Technology:** Benthic Flux Sampling Device  
**Manufacturer:** U.S. Department of Navy  
Space and Naval Warfare Systems Center,  
53560 Hull Street  
San Diego, CA 92512-5001

**Technology Description**

The Benthic Flux Sampling Device (BFSD) is a benthic lander for in-situ measurements of metal contaminant fluxes from or into shallow marine sediments. The BFSD was designed and developed by the U.S. Navy Space and Naval Warfare Systems Center, San Diego (Navy) to further characterize metal contamination problems in bays, harbors and coastal waters resulting from a variety of sources, including ships, shoreside facilities, municipal outfalls, spills and non-point source runoff. The Navy has received a U.S. Patent (#5473952) for the BFSD.

The technology provides a means to assess contaminant mobility by directly measuring and quantifying the contaminant flux across the sediment-water interface. Other techniques for estimating fluxes across the sediment-water interface rely on measurement of sediment pore water concentrations as a basis for calculating a diffusive flux. In contrast, the BFSD collects samples over time to allow a direct determination of the total flux, which may also include exchanges between sediment pore water and the overlying water from biological or other non-diffusive processes.

The BFSD collects seawater samples periodically at timed intervals from a chamber of known volume which encloses a known surface area of sediment. After a laboratory has analyzed the samples, and with knowledge of the time intervals between samples, a flux rate between the sediment and water in mass per surface area per unit time (micrograms per square meter per day [mg/m<sup>2</sup>/day]) can be calculated. A minimum deployment over three tidal cycles or 72 hours is typically used to perform a flux rate measurement which incorporates overall tidal effects. This time period is intended to balance the need to determine an overall net flux with the recognition that the presence of a benthic lander may affect the benthic environment.

The BFSD consists of an open-bottomed chamber mounted in a modified pyramid-shaped tubular framework with associated sampling gear, sensors, control system, power supply, and deployment and retrieval equipment. The entire device is approximately 1.2 by 1.2 meters from leg to leg and weighs approximately 175 pounds. The lower part of the framework contains the chamber, sampling valves, sampling bottles, and batteries. The upper frame includes a release that is acoustically burn-wire triggered. The BFSD is designed for use in coastal and inland waters to maximum depths of 50 meters. A small boat or vessel equipped with winch and cable may be used to deploy and retrieve

the BFSD. Maximum deployment time is approximately four days based on available battery capacity.

The chamber is a bottomless box, approximately 40 centimeters (cm) square by 18 cm tall, with a volume of approximately 30.0 liters. The volume was chosen to allow for a maximum overall dilution of less than 10 percent due to sampling withdrawal into 11 samples of 250 milliliters (ml) each. The chamber is constructed of clear polycarbonate to avoid disrupting any exchanges that may be biologically driven and, thus, light sensitive. To prevent stagnation in the corners of the chamber, triangular blocks of polycarbonate occupy the 90-degree angles. The top of the chamber is hinged at one edge so that it may be left open during deployment, allowing the chamber to fill with water while minimizing sediment disturbance. Once the chamber is in place, the computer control system closes the lid. A gasket around the perimeter of the chamber ensures a positive seal between the chamber and the lid. Exact alignment is not required, because the lid is slightly larger than the sealing perimeter of the gasket and pivots on two sets of hinges. The lid is held closed by four permanent magnets situated along the chamber perimeter. The bottom of the chamber forms a knife-edge. Pressure-compensated switches mounted on the bottom surface of three sides of a flange circling the chamber at 7.6 cm above the base activate a series of three lights visible with a video camera mounted on the upper frame. Illumination of the lights indicates a uniform minimum sediment penetration depth has been achieved and a good probability that a positive seal between the chamber and the sediment has been achieved.

During the deployment or sample collection period, the seawater in the flux chamber is continuously mixed and monitored for key parameters: conductivity, temperature, pressure, salinity, pH, and dissolved oxygen. Water enclosed in the flux chamber is continuously pumped through a recirculation loop including a flow-through sensor system. Mixing is accomplished as recirculated water is returned to chamber through a helical diffuser mounted vertically on the central axis of the chamber such that the hydrodynamics inside the chamber simulate near bottom currents outside the chamber.

The acquisition and control unit is an Ocean Sensors Model OS200 conductivity temperature depth (CTD) instrument, modified to allow control of the BFSD. It consists of a data logger that acquires and stores data from sensors, and a control unit that regulates sampling and other functions of the BFSD. The data logger collects data from a suite of sensors housed in the CTD and connected to the chamber through a flow-through loop. A small constant-volume pump maintains circulation in the flow-through system to the sensors and is also used to mix the contents of the chamber. The control unit closes the lid, activates the flow-through/mixing pump, activates dissolved oxygen control valves, and controls activation of the synchronized parallel rotary sampling valves.

Discrete samples are obtained using a vacuum collection approach consisting of sample containers, fill lines, in-line filters (with 0.45 micron membrane filters), check valves, and synchronized parallel rotary valves connected to the chamber fill line. Off-the-shelf 250ml Teflon collection bottles are modified to allow filling through the cap. Sampling containers of any volume, material (e.g., glass Teflon, polycarbonate), or shape may be used, provided the cap can be modified to accept the fill line connection, the bottle walls are strong enough to withstand the pressure at the sampling depth, and the cap seal is airtight and watertight at the sampling depth pressure. All valves, fittings, and tubes are made of Teflon or other nonmetallic materials to minimize potential metal contamination of samples and to facilitate cleaning. Samples are drawn from the chamber through a 4-mm Teflon tube connected to the rotary valves and into the sampling bottles. Sampling is initiated by the control system when it activates the valves at preprogrammed intervals. Seawater samples are drawn through the sampling system by a vacuum of 25 inches of mercury (minimum) which is applied to all sample bottles through

check valves mounted in the bottle lids. The check valves are then sealed. Water enters each sample bottle when the rotary valves are activated at timed intervals or when the lid closes and opens a valve attached to its hinge. Filtered seawater flows into each bottle until pressure is equalized, normally yielding at least 240ml.

An oxygen control subsystem prevents anoxic conditions from occurring within the chamber. Based on the oxygen sensor data, the system automatically adds oxygen through a 15-meter long diffusion coil in the flux chamber. The system maintains the dissolved oxygen levels in the chamber within a user-selected window about the measured bottom water oxygen level. This is done because fluxes of metal contaminants are sensitive to redox conditions and most contaminant fluxes are not large enough to be measured in chambers without oxygen regulation; the isolated volume of seawater will become anoxic before significant contaminant fluxes have occurred.

A deployment cable and release line are used to lower the BFSD to its intended depth. Following either rapid or slow descent to the bottom, the minimum depth of collection chamber insertion is sensed by pressure-compensated switches, which activate lights mounted on the chamber frame used for video monitoring and inspection of the sampling site. Recovery is accomplished by transmitting a coded acoustic signal to the frame-mounted receiver which in turn releases the marker buoy. The line attached to the buoy is used to lift the BFSD aboard the vessel. Stored sensor data is uploaded before detaching the cables.

A more detailed description of the BFSD and its components, including the sampling chamber, acquisition and control system, sampling subsystem, circulation subsystem, and oxygen control subsystem, is given in the September 1, 1999 draft report, "*Quantifying In Situ Contaminant Mobility in Marine Sediments*" prepared by Space and Naval Warfare Systems Center, San Diego (September 1, 1999 Draft Report).

## **Analytical Methods**

*Cleaning.* Prior to each deployment, the BFSD sample collection system is cleaned and decontaminated. A sequential process of flowing cleaning fluids through the sampling subsystem using vacuum; of soaking disassembled parts (collection bottles and other parts) in prepared solutions; of physically brushing and rinsing the collection and sensor chambers and the circulation subsystem with prepared solutions is followed. A nitric acid soak/rinse is used, a final rinse is carried out with 18 meg-ohm/cm de-ionized water, then all paths of contamination are sealed/closed until deployment.

*Performance Indicators.* A series of performance indicators is used to evaluate the data obtained during operational deployments. One performance indicator is the chemistry time-series data for silica. Silica, a common nutrient used in constructing the hard parts of some planktonic organisms, typically shows a continuous flux out of the sediments due to degradation processes. The linear increase in silica concentration with time in the collected sample bottles is therefore used as an internal check for problems such as a poor chamber seal at the lid or sediment surface. A field analytical test set (Hach Model DR2010) is used to assess the silica concentrations immediately following retrieval and before sending collected samples to the analytical laboratory. Also, with a good chamber seal the ongoing bacterial degradation of organic material in the sediment consumes oxygen (which must be regulated by the BFSD) and generates carbon dioxide. This gradually lowers the chamber pH. Although the expected relationships of these performance indicators aid in determining normal or

successful deployments, natural variability is always present to cloud these relationships. Variations in the pore water reactions at the various sites lead to differences in the observed fluxes of oxygen, silica, and the metals. One major factor contributing to the large variations in fluxes may be burrowing activity. Enhanced biological irrigation (pumping of the overlying seawater through sediment burrows by infaunal organisms) increases the surface area of the sediment-water interface and flow rates across the interface, and may also increase the observed fluxes. The organisms responsible for this biological pumping will also affect oxygen uptake rates and may make interpretation of the analytical results more difficult.

*Blank Tests.* As part of the performance verification, blank tests were performed by filling the BFSD with seawater and holding it in isolation from the surrounding water and sediments while samples were collected in the same manner as with sediment flux experiments. These tests were run in triplicate (triplicate blank test) to determine the lower limit of resolution for flux determinations of various metals. A polycarbonate panel was sealed across the bottom of the chamber, and the BFSD was filled with sea water as it was lowered to within several meters of the sediment surface. A standard operational program identical to the demonstration deployments was run for 70 hours. The blank test results are discussed further under the Evaluation Approach and the Field Activities and Test Results sections, below.

*Computations.* Fluxes are computed from the trace metal concentrations in each sample bottle using a linear regression of concentration versus time after the concentrations are corrected for dilution effects. These dilution effects result from the intake of bottom water from outside the chamber to replace the water removed for each collected sample. An interactive computational spreadsheet processes most data. Analytical laboratory results, sensor and other measured data, performance indicator results and blank test results are entered into the spreadsheet template and processed. A series of tables, charts and graphs are computed and displayed, including statistical confidence and other data and figures that summarize the results.

*Analytical Method.* Trace metal analyses of collected seawater for arsenic, cadmium, copper, manganese, nickel, lead, silver, and zinc in seawater, are performed by inductively coupled plasma mass spectroscopy. For the Navy field studies, Battelle Marine Science Laboratories performed the analyses using their Standard Operating Procedure, MSL-1-022-01, "Determination of Elements in Aqueous and Digestate Samples by ICP-MS." Prior to analysis, samples are preconcentrated using a published tetrahydroborate reductive precipitation technique.

## **Basis for Certification**

### *Evaluation Approach.*

The evaluation of the BFSD was designed to provide the data necessary to draw conclusions on the technology's performance. Key data regarding the technology's performance were collected during field studies performed as part of the evaluation. Additionally, the critical operating parameters and conditions related to the technology's performance, reliability and safety were to be identified. The evaluation included a review of supporting documents and information submitted by the Navy which describes their technology and its intended operation and maintenance. The Navy had previously performed tests on a prototype BFSD (Prototype BFSD), which was designed and modified as part of

their technology development and proof-of-concept efforts. DTSC reviewed these previous Navy studies to provide background on the technology and to help identify key parameters for the field studies.

The Navy conducted two field studies specifically for the certification evaluation, using the current version of the BFSD, as described in the technology description, above. These included two deployments at the Paleta Creek area of San Diego Bay, California and two deployments at the Middle Loch and Bishop Point areas of Pearl Harbor, Hawaii. The Navy conducted an additional field demonstration during the certification evaluation at the Alameda Naval Air Station, California which was also reviewed. The Department of Toxic Substances Control (DTSC) reviewed the work plans prior to the demonstrations and agreed with proposed field test objectives and procedures, and data quality objectives. DTSC staff also provided oversight and were present to observe many, but not all, of the field test activities. Following the completion of the field tests, the Navy submitted their reports providing the data collected and an analysis of the results. Detailed data submitted for the Alameda NAS site included two flux measurements. Additionally, detailed laboratory reports including QA/QC results were requested and reviewed.

The field tests were intended to verify the performance of the BFSD in quantifying the rates of exchange of target metal contaminants at the sediment-water interface. Specifically, the objectives of the BFSD technology demonstrations were to: (1) Evaluate the data to determine if a statistically significant flux was occurring at the test locations; (2) Evaluate the BFSD performance for repeatability; and (3) Evaluate a range of conditions in which the BFSD can be operated.

To determine whether statistically significant fluxes were occurring at the test locations (Objective 1), 12 seawater samples were collected at 7-hour intervals using the BFSD. The water samples were analyzed for metals including cadmium, copper, manganese, nickel, lead, zinc and silica. Sediment samples, when collected, were analyzed for grain size, total solids, total organic carbon (TOC), acid volatile sulfide (AVS), simultaneously extracted metals (SEM), and total metals. Although the sediments may have been contaminated with other constituents, only the flux of the listed metals was evaluated during the demonstrations. Sample concentrations were corrected for dilution introduced by the sample collection process, and a regression curve was generated for each analyte based on the concentration data.

To determine whether calculated fluxes are due to fluxes into or from the sediment, or due to sorption or other interactions of the metals with the BFSD components, flux rates with regression coefficients were compared with the results for each metal obtained during triplicate “blank” BFSD tests (blank tests). These blank tests were performed by filling the chamber with seawater, sealing it, and suspending it above (but isolated from) the surrounding seawater and sediment surface. The data obtained during the blank tests provided a measurement of the repeatability of metal analyses and allowed a determination of any changes in metal concentrations in seawater over time which result from the BFSD itself. The measured sediment flux rate for each metal was then evaluated to determine if a statistically significant flux had been measured when compared with the blank chamber (background) tests.

The BFSD was evaluated for repeatability (Objective 2) by analyzing the results of repeat deployments, two weeks apart, at the same Paleta Creek site. Demonstration data was also compared with data from the site during Prototype BFSD tests in the same approximate location. Finally, repeatability was evaluated by comparing the results from three blank chamber deployments. Lastly,

the range of conditions for operating the BFSF was evaluated (Objective 3) by describing the conditions under which the BFSF operated as claimed, and the projected range of contaminants applicable to the technology.

At the San Diego Bay location (Paleta Creek) two deployments at the same site were made; at the Pearl Harbor location, one deployment at each of two geologically different sites were made (Middle Loch and Bishop Point). Comparison of the results of the two Paleta Creek demonstrations to one another was intended to evaluate repeatability of the technology. Comparison of the results from the two geographically different sites in Pearl Harbor was intended to demonstrate data differences and analysis/interpretation approaches.

Three "blank test" deployments were conducted, during which the BFSF was deployed in seawater with a sealed sampling chamber. Three time series of samples were collected and a baseline was established for each analyte, which provided a statistical estimate of the lower limit of flux detection measurable with the BFSF. The data also served as another measure of repeatability. Previous results obtained at the same location using the Prototype BFSF also provided a general measure of trend repeatability. For each analyte, a rate of flux between the sediment and the water during each deployment was calculated using knowledge of the volume of water enclosed within the BFSF, the surface area of sediment isolated, the time the samples were collected, and the concentrations of the contaminants of interest in the individual samples.

At the Alameda NAS Seaplane Lagoon location the Navy measured metal contaminant fluxes in sediments at four locations in support of an ongoing site characterization study. In addition to the metal analytes mentioned above, the Navy's target metal analytes at this site included arsenic, mercury and silver. OPPTD staff were present to observe deployment and retrieval procedures for two of the deployments. A summary of the results for the four Seaplane Lagoon site deployments was reviewed in addition to the detailed data for the flux measurements made at the SPL-7 and SPL-10 locations. Laboratory reports and QA/QC results for these four flux measurements were not included in the certification evaluation.

Following the completion of the field tests, the Navy prepared a draft report "Quantifying In Situ Contaminant Mobility in Marine Sediments," September 1999, which describes the technology and discusses in detail the results of the San Diego and Pearl Harbor field tests. This report was reviewed by DTSC staff as part of the evaluation, and incorporates their comments. DTSC staff reviewed the raw data and the statistical analyses used by the Navy as the basis for the report, as well as the data obtained during the Alameda field tests.

### *Review of Previous Testing of the Technology.*

Results of previous testing and initial technology development efforts performed by the Navy were reviewed as part of the certification evaluation. Initial development program tests included ex situ (laboratory) and in situ (field) trials of critical components, subsystems, and systems. System development tests were conducted at various locations within San Diego Bay during 1989-91. Full-scale system trials during June 1991 were conducted in Sinclair Inlet, WA, including ten deployments of the Prototype BFSF to characterize flux rates of contaminants from seven shipyard sites and three reference sites (no blank test was conducted). Collected samples were analyzed for the trace metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead

(Pb) and zinc (Zn). Following review of the data, an active oxygen control subsystem with sensor feedback was developed and added to the system, along with several other changes to improve operation reliability.

During 1993, four tests of the upgraded version of the Prototype BFSD were conducted at sites within San Diego Bay: one at Paleta Creek (at its entrance to the bay within Naval Station San Diego); two at a commercial yacht harbor (Shelter Island); and one at a industrial shipping terminal (PACO Industries). The deployments were preceded by blank tests to determine the lower limits of flux that could be resolved with the Prototype BFSD. Results from these deployments showed significant sediment flux rates when compared to blank test results and clear differences between the sites as related to potential trace metal sources. Paleta Creek results showed the highest flux levels for Cd, Cu, Ni and Zn.

Seven more Prototype BFSD deployments in San Diego Bay in support of a sediment quality assessment at Naval Station San Diego were conducted during 1995. Paleta Creek was again included along with five other sites near piers and quay walls and one site outside the study area used as a reference. The work, preceded by a blank test, yielded results that were consistent with the results from the 1993 study and showed Cd, Ni, Zn and Mn all to have positive fluxes. Paleta Creek again showed the highest trace metal fluxes with levels which were generally consistent with those measured in 1993. Correlations between measured trace metal flux levels and complex marine chemistry processes were studied and informative trends were identified. For example in the complex oxidation-reduction (redox) marine environment, it was found that trace metal fluxes are consistent with oxidation of solid metal sulfides as a sediment source.

### *Field Activities and Test Results*

*Blank Tests.* The primary purpose for carrying out system blank tests was to establish BFSD minimum performance levels, or detection limits, for assessment of flux data obtained during subsequent demonstration tests. Three replicate 70-hour blank tests were conducted using BFSD between May 14 and 31, 1998. The tests were conducted from the end of SSC, San Diego Pier 159 at approximately two feet off the bottom in seawater ranging from about 14 to 20 feet deep, depending on tidal flow. As expected, the blank results for most metals showed little or no time trend, indicating minimal source or loss of target analytes during the blank experiments. With the exception of lead and manganese, replicate analysis indicates that none of the metal fluxes were significantly different from a zero flux condition at the 95% confidence level. The BFSD blank performance was statistically established and the values obtained were repeatable, precise and accurate enough to allow valid measurement of in situ sediment flux rates.

*Paleta Creek, Pearl Harbor, and Alameda NAS Demonstrations Data Assessment.* The BFSD performance assurance indicators for the flux measurements made at the three different geographic locations show that: a proper seal was achieved during the deployments and chamber isolation of test water was maintained; oxygen levels were maintained close to ambient levels; and silica, oxygen and pH trends varied as expected. The flux measurements at these sites for the target metals, arsenic, cadmium, copper, lead, nickel and zinc, were determined to be statistically different from the blank, indicating actual fluxes of these metals from or into the sediments were occurring. Data for cadmium, copper, lead, nickel and zinc were obtained from all three field tests, while data for arsenic

was obtained only from the tests at Alameda NAS. The results for arsenic, however, showed a high level of confidence (>99%) that the calculated fluxes at this site were statistically different from the blank flux. Additional details and discussion of the results for the San Diego and Pearl Harbor field tests are available in the Navy's report "Quantifying In Situ Contaminant Mobility in Marine Sediments," September 1999. Supporting data for the Alameda field tests are available in the project files.

### *QA/QC Review*

As part of certification evaluation, the DTSC Hazardous Materials Laboratory reviewed the laboratory data packages for 10 selected trace metal analyses performed by Battelle Marine Science Laboratories (Battelle). Review was based on Battelle's Standard Operating Procedure (SOP), MSL-1-022-01, "Determination of Elements in Aqueous and Digestate Samples by ICP-MS." The review found that due to possible contamination of the method blanks, some Mn and one copper result should be rejected. Additionally, the review found certain results for Cr, Co, Pb, Sb, Ag and Sn associated with QA/QC results outside the control limits should be used with caution. All other metal results reviewed were found acceptable.

### *Conclusions*

1. The deployments of BFSD at the Paleta Creek, Pearl Harbor, and Alameda NAS demonstrated consistent performance, reliability, and the ability to measure trace metal fluxes at distinctly different sites.
2. The BFSD can provide accurate and repeatable measurements of the mobility of trace metal contaminants to and from shallow water marine sediments when certain prerequisite conditions are met. Statistically significant sediment flux rates can be established when the routine procedures, standard methods and protocols demonstrated during this study are followed. Comparison of measured sediment fluxes with blank-chamber fluxes provides a statistical benchmark for the significance of the measured flux rates. Where statistically significant fluxes are observed, evaluation of impacts on water quality can be carried out, or comparisons can be made to bioaccumulation measurements to help identify exposure pathways.
3. Measurement of manganese flux rates is problematic. The flux rate measured over time does not appear to be linear, possibly due to precipitation chemistry occurring with manganese within the flux chamber. The validity of using the first several time series concentration measurements to determine the flux for manganese was not clearly established.
4. A statistical comparison of the field-measured flux rate to the blank-chamber flux rate is necessary to establish a confidence level (e.g., 80%) that the sediment flux is different from the background variability observed under a no-flux condition. Confidence levels less than 80% indicate that the flux may not be detectable and that the results should be used with caution.

5. The best-fit linear flux rate generally provides the best estimate of the flux from the data. The measured statistical variation in the flux should be reported in terms of the slope of the linear regression line and the 95% confidence limits of the slope.
6. The data obtained from use of this technology should be interpreted by persons who are technically qualified to assess sediment fluxes and who are familiar with the site-specific applicability of the BFSD.

### **Certification Statement**

Under the authority of Health and Safety Code section 25200.1.5, the Benthic Flux Sampling Device (BFSD), an automated, in situ, water sampling device designed to collect data to quantify the flux of contaminants across the sediment-water interface in marine and aquatic environments, is hereby certified as a site characterization technology subject to the specific conditions including the limitations/disclaimer set forth in the Certification Notice as published in the California Regulatory Notice Register on **[month, day, year]**, Register No. **[xx]**, Volume No. **[xx-Z]**, pages **[xxxx - xxxx]**.

The BFSD, an autonomous benthic chamber lander, encloses a volume of water in an open-bottom chamber over approximately 0.2 square meters of sediment; discrete water samples are collected periodically over a deployment period of up to four days, preserved at the end of the deployment, and delivered to an analytical laboratory for analysis. With knowledge of the sediment surface area, the volume of water, the time the samples are collected, and the concentrations of constituents in the samples, a flux, expressed in mass per unit area per time, can be derived. The method, and resulting data, are valid when the BFSD standard operating procedures, the laboratory quality assurance and control procedures, and the internal quality assurance checks, such as silica flux, oxygen and pH stability, and statistical tests, have been met. The BFSD is capable of:

1. Deployment from a small surface craft using light duty handling equipment;
2. Operation in a marine environment at depths to 20 meters and bottom currents to two knots;
3. Remote real-time video imaging of the bottom site prior to autonomous operations;
4. Programmable, microprocessor-controlled autonomous operation for up to 96 hours;
5. Placement (bottom landing) with minimal disturbance of bottom sediments;
6. Isolation and maintenance of homogenous conditions in approximately 30 liter volume of bottom water for the period of sample collection;
7. Maintenance of oxygen content in the sample chamber within two milliliters per liter (ml/L) of initial conditions;
8. Collection of up to twelve 250 milliliter water samples from the chamber at selected intervals;
9. Measurement and storage of sample chamber depth, dissolved oxygen, pH, conductivity/salinity, and temperature data at selected intervals throughout deployment;
10. Recovery using a portable acoustic signal device to activate a tethered marker buoy;
11. Quantification of flux rates for Arsenic, Cadmium, Copper, Nickel, Lead, and Zinc based on a least-squares, linear regression of concentrations from six to 12 samples;
12. Identification of statistically significant flux rates based on comparison of sediment flux rates measured at the site to flux rates measured in a “blank” BFSD chamber containing sea water isolated

from the sediment;

13. Blank BFSD chamber performance meeting the following performance standards:

Metal	Blank Flux (ug/m2/day)	+/- 95% Confidence Interval
Arsenic	-5.16	2.10
Cadmium	-.052	0.75
Copper	2.82	8.73
Nickel	10.28	7.34
Lead	3.16	1.59
Zinc	-3.38	65.22

14. Verification of proper flux chamber seal and sample collection based on silica concentrations within the chamber during the measurement period;

15. Identification of environmentally significant fluxes on the basis of comparisons/relations such as:

- a. other known contaminant sources
- b. hydrodynamic flushing rates of the basin
- c. remobilization due to other mechanisms such as sediment resuspension
- d. fluxes measured prior to placement of a containment system such as a cap
- e. fluxes measured prior to removal of contaminated sediments
- f. bioaccumulation in marine organisms at the site
- g. mass balance analysis of input and loss rates for sediment

### **Specific Conditions**

1. Limitation to Specific Metals and Operating Conditions. The certification of the BFSD is specific to flux measurements of arsenic, cadmium, copper, nickel, lead, and zinc under the specified operating conditions. The performance with other metals or under different operating conditions was not addressed as part of the certification evaluation.
2. Requirement for Blank Tests. Except where water quality conditions are equivalent to those where blank test performance has previously been verified for seawater in the BFSD isolated from the sediment, BFSD blank tests shall be performed in accordance with the Navy's procedures to determine the lower limit of resolution for metal flux measurements. Additionally, blank test performance shall be verified for each new BFSD manufactured.
3. Reporting of measured flux rates should include the slope of the best-fit linear regression line (the linear flux rate), the 95% confidence limits of the slope (the measured statistical variation in the

flux) and, for statistical comparison purposes, corresponding results of the triplicate blank tests. The statistical confidence level that the field-measured flux rate is measurably different from the blank-chamber flux rate shall also be reported. Flux measurement results should be reported as non-detectable or otherwise flagged when there is a confidence level of less than 80% that the benthic flux measurement is different from the blank flux measurement.

4. Operational Procedures. Users of the BFSD should follow the operational and maintenance procedures developed by the Navy. The procedures for operation, maintenance, sample collection and analysis, and data assessment are set forth in the *September 1999 draft Report*.
5. Compliance with Worker Health and Safety Laws. Operation of the BFSD must be in compliance with applicable federal, state and local regulations relating to the protection of worker health and safety.
6. Personnel Training. The operator shall be properly trained on how to operate the BFSD safely and effectively.
7. Compliance with Applicable Federal, State, Local Regulations. The user shall comply with all applicable federal, state, and local regulatory requirements.
8. Continuous Quality Control/Quality Assurance and Monitoring by DTSC. By accepting this certification the applicant agrees, for the duration of the certification, that the BFSD and its operation and maintenance and other documentation shall be maintained at a quality equal to or better than that in place at the time of certification. The applicant also agrees to be subject to monitoring by DTSC.
9. Modifications and Amendments at the Request of the Applicant. Modifications and amendments to this certification may be requested by the applicant and will be subject to approval by DTSC.
10. Certification Reference. The holder of a valid hazardous waste environmental technology certification is authorized to use the certification seal (California Registered Service Mark Number 046720) and shall cite the certification number and date of issuance in conjunction with the certification seal whenever it is used. When providing information on the certification to the user of the technology or another interested party, the holder of a hazardous waste environmental technology certification shall at a minimum provide the full text of the final certification decision as published in the California Regulatory Notice Register.

## **Regulatory Implications**

There are currently no standards or approved procedures developed by regulatory agencies for use of benthic landers, such as the BFSD, for measurement of contaminant metal flux. Although some clean water standards have been set for seawater, only guidelines currently exist for sediments. The interpretation and application of metal flux measurements with the BFSD is very site-specific and does

not lend itself readily to standardized processes. In many cases, BFSD results may be used as an additional factor in a "weight of evidence" approach for risk-based decisions involving regulator concurrence.

### **Duration of Certification**

This certification will remain in effect for three years from the date of issuance, unless it is revoked for cause or unless a duration for certifications different from that specified in this certification is adopted in regulations.